

PATENT
Attorney Docket No. 08009.0010-00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)	
)	
Katsuya KASE et al.)	Group Art Unit: 1745
)	
Application No.: 10/781,624)	Examiner: K. O'Neill
)	
Filed: February 20, 2004)	Confirmation No.: 4112
)	
For: ACTIVE MATERIAL FOR)	VIA EFS-WEB
POSITIVE ELECTRODE IN NON-)	
AQUEOUS ELECTROLYTE)	
SECONDARY BATTERY)	

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION UNDER 37 C.F.R. § 1.132

I, Katsuya KASE, do hereby make the following declaration:

1. I am a Japanese Citizen, residing at 17-3, Isoura-cho, Niihama-shi, Ehime-ken, Japan.
2. I have been awarded a Master of Science from Chiba University, Japan.
3. I have been employed by Sumimoto Metal Mining Co., and its predecessor corporations since April 1, 1992, and I am presently Manager of the Technical Section of the Battery Department. During my employment at Sumimoto Metal Mining Co., I have been with the Advanced Materials Division, Isoura Plant.
4. I have read and understand the rejections presented in the Final Office Action mailed September 8, 2008, in U.S. Patent Application No. 10/781,624, and the reference cited therein, Japanese Publication No. JP 2000-021402. In my opinion, a

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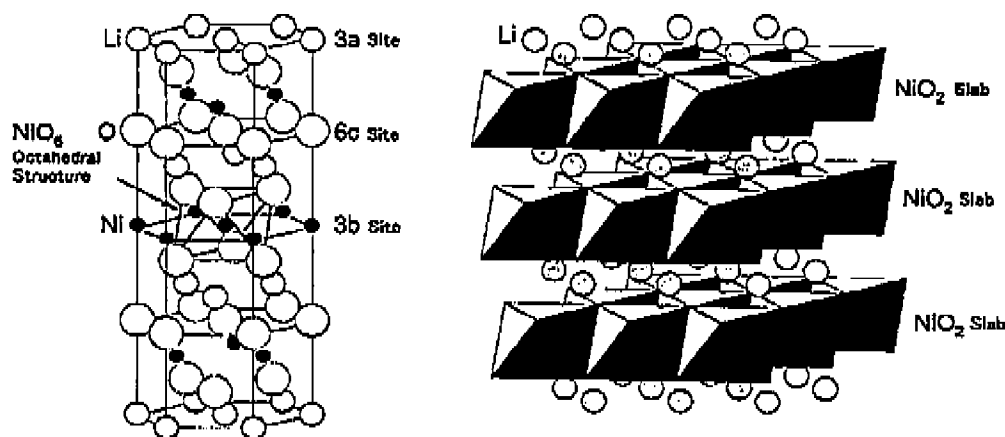
person of ordinary skill in the art of active materials for secondary batteries would recognize that Japanese Publication No. JP 2000-021402 does not disclose a lithium composite oxide that inherently possesses a lithium occupancy rate of 98% or more, or a carbon amount of 0.12 weight % or less.

6. Given my education and experience, particularly in the area of battery compositions and manufacturing, I consider myself able to provide the following testimony regarding the knowledge of one of ordinary skill in the art regarding certain lithium ion battery technology, as well as the following experiments conducted by me or under my supervision.

7. As described, for example, in Paragraph 0018 of JP H11-25980, a lithium nickel composite oxide (LiNiO_2) having a hexagonal layered structure has certain sites (i.e., 3a, 3b, and 6c sites) for the disposition of each element.¹ If such an oxide has a completely stoichiometric composition, 100% site occupancy rate is shown for Li, Ni, and O for each of the 3a, 3b, and 6c sites, respectively. For illustrative purposes, a model of the crystal structure of a lithium nickel composite oxide having a hexagonal layered structure is as follows:

¹ A copy and machine translation of JP H11-25980 is being submitted with the filing of this Declaration.

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8. Although Li ions have small ionic radius relative to other elements, their presence in such a hexagonal structure is limited to the 3a sites, because lithium atoms cannot be disposed in every position of the crystal structure. Thus, a lithium composite oxide having a completely stoichiometric (i.e., 100% site occupancy rate) is only obtained when the lithium ions completely enter and occupy the 3a sites of the crystal (i.e., when lithium ions completely occupy all of the 3a sites).

9. As described in Paragraph 0009 of JP H11-25980, charging and discharging is carried out in such a crystal by the reversible leaving and entering of Li ions that are sandwiched between NiO_2 slabs (NiO_2 layers formed from NiO_2 octahedral structures that share the ridge line thereof). As a result, the oxide can function as an active material for a positive electrode.

10. As described in Paragraphs 0004 and 0005 of JP H11-25980, however, it is difficult to obtain a lithium nickel composite oxide having a desired stoichiometric composition. That is, it is difficult to produce a lithium nickel composite oxide having a high lithium site occupancy rate (and thus, a high degree of stoichiometry). This is

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because Ni^{3+} ions are unstable, and because the non-stoichiometric $\text{Li}_x\text{Ni}_{1-x}\text{O}_2$ ($0 < x < 1$) oxide is readily formed. See Thomas et al., Mat. Res. Bull., 20, 1137 (1985).

11. Further, even if a lithium nickel composite oxide has excellent stoichiometry, it may have less than optimum cycling characteristics. This is because the crystallinity of the oxide degrades as Li ions disintercalate. This degradation results from the cooperative Jahn-Teller distortion of nickel ions, which converts the NiO_2 slabs in the crystal into a form through which it is difficult to charge and discharge (i.e., intercalate and disintercalate Li^+ ions).

12. In the Final Office Action dated September 8, 2008, the Office asserts that the lithium site occupancy rate of lithium composite oxide disclosed in JP 2000-21402 ("Inoue") will exceed 98 %, because lithium is present in the material in a ratio of 0.99 to 1.10. The Office asserts that this range is close to a stoichiometry of 1, and indicates that the small size of Li ions would allow them to occupy more space in the lattice work of the active material than any other reactant.

13. However, the mere fact that the atomic ratio of lithium in the compound falls within 0.99 to 1.10 does not necessarily mean that the lithium site occupancy rate will exceed 98% in the crystal. Indeed, metals other than lithium can occupy the lithium 3a sites in the crystal, thereby lowering lithium site occupancy. Moreover, to obtain a lithium composite oxide having a high degree of stoichiometry and excellent crystal structure, the manufacturing conditions (including the raw materials) used to produce the oxide must be controlled. To demonstrate this fact, the following experiments were conducted.

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14. Three nickel composite oxides, A, B, and C, were produced. The composition of these samples was as follows.

Sample	Nickel Content	Cobalt Content	Aluminum Content	Concentration of SO ₄ ions	Average Particle Size
A	63.2 wt%	12.0 wt%	1.3 wt%	0.7 wt%	8.2 μm
B	63.2 wt%	11.9 wt%	1.3 wt%	1.0 wt%	8.3 μm
C	63.3 wt%	11.9 wt%	1.3 wt%	1.5 wt%	8.2 μm

As shown, these nickel composite oxides correspond to the nickel compound containing element N described in Paragraphs [0030]-[0037] of Inoue. That is, the nickel oxide is substituted for cobalt compound (cobalt oxide) of Example I of Inoue.

15. To 100 g of each of the samples, 52.6 g of commercially sold lithium carbonate anhydrous powder (Average Particle Size: 62.3 μm, Concentration of SO₄ ions: < 0.01 wt%) was mixed, resulting in raw material mixtures in which the atomic ratio of Li / (Ni + Co + Al) of about 1.07. The lithium carbonate anhydrous powder corresponds to the lithium compound described in Paragraph [0030] of Inoue and to the lithium carbonate powder of Example I of Inoue. In addition, the mixture ratio of the raw material mixtures falls within the defined range described in Paragraph [0031] of Inoue.

16. Each of the raw material mixtures was sintered in oxygen airflow (100 % of oxygen) for 4 hours at 250 °C, 9 hours at 450 °C and 22 hours at 730 °C, and the sintered body was cooled to room temperature. These sintering conditions are consistent with those described in paragraphs [0034] and [0035] of Inoue.

17. Each sintered body was then crushed in nitrogen atmosphere using a pin mill, and screened using an ultrasonic vibrating screen and a wind classifier to obtain a powder having average particle size of 1 μm to 25 μm. The obtained powders were vacuum-dried for 24 hours at 150 °C. This particle size is consistent with the range

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described in paragraph [0037] of Inoue.

18. X-ray diffraction analysis was performed on the obtained lithium nickel composite oxides, and it was confirmed that each oxide had a hexagonal layered structure. The chemical composition of the obtained lithium nickel composite oxides is provided in the following table:

Sample	Lithium Content	Nickel Content	Cobalt Content	Aluminium Content	Concentration of SO ₄ ions
A	7.5 wt%	48.3 wt%	9.1 wt%	1.0 wt%	0.6 wt%
B	7.8 wt%	48.3 wt%	9.0 wt%	1.0 wt%	1.1 wt%
C	7.6 wt%	48.4 wt%	9.1 wt%	1.0 wt%	1.1 wt%

Each of these samples fall within the composition range defined in claim 1 and paragraph [0021] of Inoue, and has a concentration of SO₄ consistent with the range described in Claim 2 of Inoue.

19. The above-described synthesis was performed in accordance with the Office's opinion in the Final Office Action dated September 8, 2008. It is also consistent with the method described in paragraphs [0030]-[0037] of Inoue, where a nickel hydroxide solution was not used and a lithium carbonate and a nickel oxide were used as raw materials. Thus, I believe that a meaningful comparison between the invention described in U.S. Application No. 10/781,624 and these samples can be made.

20. With this in mind, the lithium site occupancy rate of samples A, B, and C was obtained via the X-ray diffraction chart using Rietveld analysis. The results are provided in the following table:

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Sample	Lithium Site Occupancy Rate	Carbon Amount
A	94.7 %	0.22 Wt%
B	93.8 %	0.31 Wt%
C	93.0 %	0.38 wt%

21. As shown, samples A, B, and C, which were manufactured in accordance with the Office's opinion and the method described in Inoue, exhibit a lithium site occupancy rate significantly less than 98%, and a carbon content significantly greater than 0.12 weight %.

22. I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: 9. Feb. 2009

By: Katsuya Kase
Katsuya KASE

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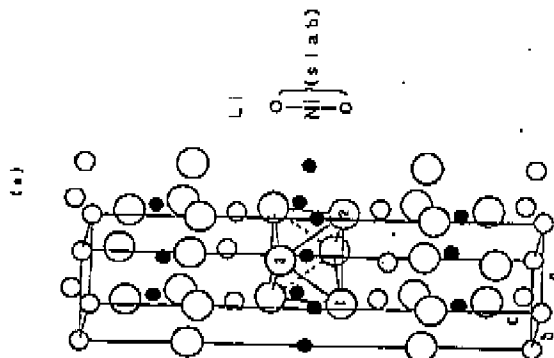
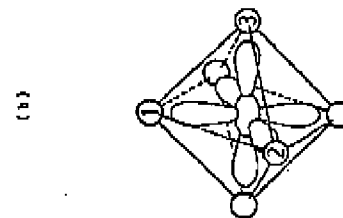
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(54) 【発明の名称】 非水系電解質二次電池用正極活物質およびその評価方法

(57) 【要約】

【課題】二次電池のサイクル特性を向上（放電容量を維持）させることが可能なりチウムニッケル複酸化物を提供する。

【解決手段】式： $[L\ 1] 3a [Ni_{1-x-y}Co_xM_y] 3b [O_2] 6c$ で表わされ、かつ層状構造を有する六方晶系のリチウム複酸化物において、X線回折のリートベルト解析結果からえられた原子位置座標より3bサイトの金属原子を中心とした酸素八面体の歪みODP= do-o, intra/ do-o, inter（ただし、do-o, intraはa軸とb軸とで作られる面内の酸素原子間距離：do-o, interは面外の酸素原子間距離）を求めた場合、該ODP値が1.065以下になることを特徴とする。



* NOTICES *

JP0 and INPIT are not responsible for any
damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]formula: $[\text{Li}]_3\text{a}[\text{nickel}_{1-x-y}\text{Co}_x\text{M}_y]_3\text{b}[\text{O}_2]_6\text{c}$ — here, The addition $x:0.05 \leq x \leq 0.25$ of $0.75 < 1-x-y < 0.90$ cobalt, the addition $y:0 \leq y \leq 0.15$ of the metal M, and a subscript of \square express a site.

In a lithium multiple oxide of a hexagonal system which comes out, is expressed and has the layer structure. Distortion of centering on metal atom of 3b site oxygen [coordinates / which were acquired from the Rietveld analysis result of an X diffraction / atom position] octahedron (ODP=Octahedral Distortion Parameter)

ODP= $d_{\text{do-o}}$, intra/ $d_{\text{do-o}}$, and inter — however, Positive active material for nonaqueous electrolyte secondary cells characterized by this ODP value becoming 1.065 or less when $d_{\text{do-o}}$, distance $d_{\text{do-o}}$ between oxygen atoms within a field where intra is made from an a-axis and a b-axis, and inter find distance between oxygen atoms outside a field.

[Claim 2]The positive active material for nonaqueous electrolyte secondary cells according to claim 1 which is characterized by a grating constant of an a-axis obtained in the Rietveld analysis being 2.863–2.865 Å in the case of $y=0$.

[Claim 3]The positive active material for nonaqueous electrolyte secondary cells according to claim 1, wherein the metal M is Mn and an ODP value is 1.060 or less.

[Claim 4]The positive active material for nonaqueous electrolyte secondary cells according to claim 1, wherein the metal M is aluminum and an ODP value is 1.058 or less.

[Claim 5]In a lithium nickel multiple oxide whose seat share of a non-lithium ion of 3a site is 2% or less in the Rietveld analysis result have a hexagonal type and according to an X diffraction, The positive active material for nonaqueous electrolyte secondary cells according to claim 3 or 4, wherein ratios (c/a) of a c axis grating constant to an a-axis grating constant are 4.94 or more and 4.96 or less.

[Claim 6]The positive active material for nonaqueous electrolyte secondary cells according to claim 3, 4, or 5, wherein a grating constant of an a-axis obtained in the Rietveld analysis is 2.855–2.870 Å.

[Claim 7]In a lithium multiple oxide of a hexagonal system which has the layer structure according to claim 1, Distance between oxygen atoms within a field made from an a-axis and a b-axis from atom position coordinates acquired from the Rietveld analysis result of an X diffraction () [$d_{\text{do-o}}$ and] Distance between oxygen atoms outside a field which sandwiched a layer of a metal atom of intra and 3b site () [$d_{\text{do-o}}$ and] A valuation method of positive active material for nonaqueous electrolyte secondary cells calculating inter and judging propriety of this lithium multiple oxide system active material by distortion (ODP) of oxygen octahedron centering on a metal atom of 3b site.

[Claim 8]A valuation method of positive active material for nonaqueous electrolyte secondary cells characterized by a thing it is [a thing] suitable as an active material in the valuation method according to claim 7 if an ODP value is 1.065 or less, and to judge.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention]This invention relates to the positive active material of the nonaqueous electrolyte secondary cell which uses lithium, a lithium alloy, or carbon for a negative electrode, and relates to high-capacity-izing of a cell, and the improvement in a cycle characteristic (maintenance of high capacity) especially by improvement of positive active material. It is related with the valuation method of the above-mentioned positive active material.

[0002]

[Description of the Prior Art]In recent years, development of the small size which has a high energy density, and a rechargeable battery with lightweight and high capacity is strongly desired with the spread of portable devices, such as a cellular phone and a notebook sized personal computer. There is a rechargeable lithium-ion battery which uses lithium, a lithium alloy, or carbon as a negative electrode as such a thing, and research and development are done briskly. Since 4V class high voltage is obtained, the rechargeable lithium-ion battery which used for positive active material the lithium cobalt double oxide (LiCoO_2) in which composition is comparatively easy is expected as a cell with high energy density, and utilization is following it.

[0003]However, in order to use an expensive cobalt compound for a raw material, that there is a unit price per capacity by about 4 times of a nickel hydride battery etc. causes a cost hike of an active material and also a cell. Therefore, the use applied is limited considerably. In the light weight of the portable device which has spread now, and a miniaturization, it has a big meaning industrially to lower the cost of an active material and for manufacture of a cheaper lithium cell to be attained.

[0004]The lithium nickel multiple oxide (LiNiO_2) using nickel cheaper than cobalt as a material with new positive active material of a lithium cell can be mentioned. In order that this lithium nickel multiple oxide may show electrochemical potential lower than a lithium cobalt double oxide, since decomposition by oxidation of an electrolysis solution cannot become a problem easily, high capacity can be expected, and development is performed briskly. However, the thing excellent in stoichiometry is hard to be obtained, and this lithium nickel multiple oxide is made difficult [composition]. . This is for nickel³⁺ to be unstable and to tend to take non-stoichiometric composition $\text{Li}_x\text{nickel}_{1-x}\text{O}_2$ ($0 < x < 1$) at an elevated temperature. (For example, M.G.S.G. Thomas et al, Mat. Res. Bull., 20, 1137 (1985)). Although it is avoidable by using the material which was rich in the reactivity of lithium peroxide, nickel nitrate, etc. as a raw material, since handling is difficult for this problem and it is expensive as an industrial source, it cannot attain the purpose of low-cost-izing. [of handling]

[0005]Also in the lithium nickel multiple oxide excellent in this stoichiometry, there is a problem in a cycle characteristic, and as this cause. When Li ion deintercalates, crystallinity falls by common yarn teller distortion of nickel ion, and it is reported that charge and discharge transfer to a difficult crystal phase (for example, the Sugano ****, the electrochemistry 63, No.7, 778 (1995)).

[0006]The fundamental characteristic of such an active material is estimated by actually making a cell as an experiment and measuring capacity. It is necessary for the charge and discharge test of one cycle to be insufficient as evaluation of an active material, since there is a problem in a cycle characteristic, and to repeat tens or more cycles, and to also evaluate the maintenance factor of capacity. For this reason, the characteristic which was excellent in the lithium secondary battery with large capacity became an evaluation test of the active material with the adverse element, and there was a problem that characterization will take a long time.

[0007]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the lithium nickel multiple oxide which can raise the cycle characteristic of a rechargeable battery (service capacity is maintained). The appraisal method which can judge the propriety of an active material promptly and correctly is offered a technical problem.

[0008]

[Means for Solving the Problem]In order to solve the above-mentioned problem, this invention persons found out that a close relation between a crystal structure and a cycle characteristic which were searched for from a powder X diffraction was, as a result of advancing various researches. If a crystal

structure of this active material is shown typically, it will become like drawing 1 (a).

[0009]Although a NiO_2 layer formed from NiO_6 octahedron which shares especially an Imperial mausoleum is called slab, (A. G. Delmas) [Rougier,] and A.V. Chadwick, Solid State Commun., and 94 [2] (1995) 123-127. — a charge-and-discharge reaction of a cell advances and it acts as an active material because Li ion sandwiched with this slab goes in and out reversibly. Therefore, I thought that NiO_2 slab structure served as an indicator big when getting to know the stability of an active material under cell reaction. Then, in order to attain an aforementioned problem, as a result of advancing research variously, it found out that a close relation between structure of oxygen octahedron and a cycle characteristic which are shown in drawing 1 (b) centering on nickel Ni atoms in slab was. Although written on a regular octahedron in a figure, since length differs, before Li ****s, in distance (face-to-face) of distance (inside of a field made from an a-axis and a b-axis) of the oxygen 1 and the oxygen 2, the oxygen 1, and the oxygen 3, this octahedron is distorted in practice. When this distortion took a certain value, change of a crystal structure was small at the time of charge and discharge, and it was imagined as what a lithium ion frequents easily. [0010]As a result, it turned out by asking for distortion of oxygen octahedron centering on nickel Ni atoms (metal atom of 3b site) from a result of X diffraction Rietveld analysis that evaluation of an active material is possible, without doing a cell examination in a lithium nickel multiple oxide excellent in stoichiometry. [0011]namely, this invention — formula: $[\text{Li}]_3\text{a}[\text{nickel}_{1-x-y}\text{Co}_x\text{M}_y]_3\text{b}[\text{O}_2]_6\text{c}$ — here, The addition $y:0<y\leq 0.15$ of the addition $x:0.05\leq x\leq 0.25$ metal M of $0.75<1-x-y\leq 0.90$ cobalt and a subscript of [] express a site.

[0012]In a lithium multiple oxide of a hexagonal system which comes out, is expressed and has the layer structure, Distortion of centering on metal atom of 3b site oxygen [coordinates / which were acquired from the Rietveld analysis result of an X diffraction / atom position] octahedron (ODP=Octahedral Distortion Parameter)

$\text{ODP}=\text{do-o}$, $\text{intra}/\text{do-o}$, inter , however do-o , Distance between oxygen atoms within a field where intra is made from an a-axis and a b-axis, do-o , and inter are the positive active material for nonaqueous electrolyte secondary cells, wherein this ODP value becomes 1.065 or less, when distance between oxygen atoms outside a field is found.

[0013]In the above-mentioned active material, it is the above-mentioned positive active material for nonaqueous electrolyte secondary cells, wherein a grating constant of an a-axis obtained in the Rietveld analysis is 2.863–2.865 Å. This idea can be applied also when adding Co and Mn (M=Mn) for improvement in a cycle characteristic, and it serves as an indicator which acquires the higher addition effect.

[0014]namely, this invention — formula: $[\text{Li}]_3\text{a}[\text{nickel}_{1-x-y}\text{Co}_x\text{M}_y]_3\text{b}[\text{O}_2]_6\text{c}$ — here, in $0.75<1-x-y\leq 0.90$, $0.05\leq x\leq 0.25$, $0<y\leq 0.15$, and a lithium multiple oxide of a hexagonal system which comes out, is expressed and has the layer structure, It is the positive active material for nonaqueous electrolyte secondary cells, wherein distortion of oxygen octahedron centering on a metal atom of 3b site (ODP value) becomes 1.060 or less from atom position coordinates acquired from the Rietveld analysis result of an X diffraction. Because of improvement in a cycle characteristic, this idea can be applied, also when it is M=aluminum, and it serves as an indicator which acquires the higher addition effect.

[0015]namely, this invention — formula: $[\text{Li}]_3\text{a}[\text{nickel}_{1-x-y}\text{Co}_x\text{Al}_y]_3\text{b}[\text{O}_2]_6\text{c}$ — here, in $0.75<1-x-y\leq 0.90$, $0.05\leq x\leq 0.25$, $0<y\leq 0.15$, and a lithium multiple oxide of a hexagonal system which comes out, is expressed and has the layer structure, It is the positive active material for nonaqueous electrolyte secondary cells, wherein distortion of oxygen octahedron centering on a metal atom of 3b site (ODP value) becomes 1.058 or less from atom position coordinates acquired from the Rietveld analysis result of an X diffraction.

[0016]In a lithium nickel multiple oxide whose Rietveld analysis result have a hexagonal type and according to an X diffraction is above-mentioned M=Mn or aluminum whose seat share of a non-lithium ion of 3a site is 2% or less, It is the positive active material for nonaqueous electrolyte secondary cells, wherein ratios (c/a) of a c axis grating constant to an a-axis grating constant are 4.94 or more and 4.96 or less. It is the above-mentioned positive active material for nonaqueous electrolyte secondary cells, wherein a grating constant of an a-axis obtained in the Rietveld analysis is 2.855–2.870 Å.

[0017]formula: $[\text{Li}]_3\text{a}[\text{nickel}_{1-x-y}\text{Co}_x\text{M}_y]_3\text{b}[\text{O}_2]_6\text{c}$ This invention is corrected, In a lithium multiple oxide of a hexagonal system which is expressed with $0.75<1-x-y\leq 0.90$, the addition $x:0.05\leq x\leq 0.25$ of Co, and the addition $y:0<y\leq 0.15$ of the metal M, and has the layer structure, It is the distance between oxygen atoms within a field () from atomic coordinates acquired from the Rietveld analysis result by an X diffraction. [do-o and] Distortion (ODP) of centering on metal atom of 3b site oxygen [find distance

between oxygen atoms outside a field which sandwiched a layer of a metal atom of intra and 3b site (do-o, inter), and] octahedron

It is an appraisal method by which it is judging-by $ODP = \frac{do-o, intra}{do-o, inter}$ and inter-propriety of this lithium multiple oxide system active material characterized. If said ODP value is furthermore 1.065 or less, it is a valuation method of positive active material for nonaqueous electrolyte secondary cells judging that it is suitable as an active material.

[0018]

[Embodiment of the Invention]The Rietveld analysis according [examination of a crystal structure and stoichiometry] to an X diffraction. It can carry out using (for example, R.A. Young, ed., The Rietveld Method, Oxford University Press, (1992)), This analysis can ask for the site share of each ion used as the index of the completeness (stoichiometry) of a crystal other than a grating constant.

[0019]In the case of the compound of a hexagonal system, there is a site of 3a, 3b, and 6c, and in being perfect stoichiometric composition, as for Li and 3b site, in 3a site, O shows the seat share of 100%, respectively, as for nickel and 6c site. It can be said that the lithium [of as / whose seat share of the Li ion of 3a site is not less than 98%] nickel multiple oxide is excellent in stoichiometry. If it puts in another way, it can be said that the lithium [of as / whose mixing rate of metal ions other than the Li ion to 3a site is 2% or less] nickel multiple oxide is excellent in stoichiometry.

[0020]In a lithium [of as / whose seat share of the Li ion of 3a site is not less than 98%] nickel multiple oxide, if NiO_2 slab structure is stable, deterioration/disassembly of the active material resulting from

change of the crystal structure at the time of charge can be suppressed. That is, if there is little distortion of the oxygen octahedron centering on the nickel Ni atoms which form slab, even if it will repeat the cycle of charge and discharge, it is a good active material with little capacity deterioration.

[0021]When it thinks as battery active material, the completeness of a crystal can be maintained even if Li deficit produces it, since it can **** and Li can be inserted. Therefore, it is considered to be a good method that stoichiometry or the completeness of a crystal is actually shown with the mixing rate of the non-lithium ion of 3a site.

[0022]The active material of this invention is positive active material for nonaqueous electrolyte secondary cells whose distortion (ODP) of the oxygen octahedron in NiO_2 slab structure is 1.065 or less in the above-mentioned lithium nickel multiple oxide and whose grating constant of an a-axis is 2.863-2.865 Å.

[0023]the active material of this invention --- some nickel of the above-mentioned lithium nickel multiple oxide --- Co and Mn --- or, It is the lithium nickel multiple oxide replaced with Co and aluminum, and the distortion (ODP) of the oxygen octahedron in NiO_2 slab structure is 1.058 or less, And the grating constant of an a-axis is 2.855-2.870Å, and the ratio (c/a) of a c axis grating constant to an a-axis grating constant is the positive active material for nonaqueous electrolyte secondary cells which is 4.94 or more and 4.96 or less.

[0024]

[Example]

- Example 1-[composition of active material sample] lithium hydroxide ($LiOH \cdot H_2O$: 99% of purity), and formula: $(nickel_{1-x}Co_xM_y)In(OH)_n$. The nickel cobalt coprecipitation hydroxide prepared so that x and y might become a value shown in ** thru/or ** of the following, respectively. Weighing is carried out so that lithium [/] (nickel + cobalt) atomic ratio may serve as a predetermined value respectively shown in ** thru/or ** of the following, Those total weight of 3.4 kg was mixed for 5 minutes using the mixing granulation machine (the product made from Fukae Industry: high speed mixer). 430 cc of PVA solution was added 2 more%, and the granulation was performed for 10 minutes. Next, after collecting granulation things and drying at 100 ** for 2 hours, it compounded by heating this to prescribed temperature and holding it with the heating rate at 300 **/h in the atmosphere of 3.0 l. of oxygen flow rates / min, for 15 hours using a magnesia setter.

[0025]** Example 1-1. x= 0.08, y= 0, Li/. (nickel+Co) =1.1 and the synthesizing temperature =700 ****

example 1-2. x= 0.16, y= 0, Li/. (nickel+Co) =1.05, synthesizing temperature =680 **** example 1-3

x=0.16, y= 0, Li/(nickel+Co) =1.05, synthesizing temperature =700 **** example 1-4 x=0.16, y= 0, Li/

(nickel+Co) =1.05, and the synthesizing temperature =720 **** comparative example 1-1. x= 0.17, y= 0,

Li/(nickel+Co) =1.05, synthesizing temperature =750 **** comparative example 1-2 x=0.17, y= 0, Li/

(nickel+Co) =1.10, synthesizing temperature =750 **** comparative example 1-3 x=0.15, y= 0, Li/

(nickel+Co) =1.05, synthesizing temperature = 650 ** [0026][X diffraction] The X-ray diffraction pattern of

each sample was measured using the X-ray diffractometer (RADrVB) made from Physical science. By CuK

alpha rays (tube voltage of 40 kV, 150 mA of tube current), measuring conditions are sampling 0.02 degree in width, and the scan speed of 4.00 degrees / min. and considered the slit as 1.00 degrees of emissions, and 0.3 mm of 1.00 degrees of dispersion light-receiving, respectively.

[0027]The X-ray diffraction pattern was analyzed based on them [R3] crystal model using Rietveld analysis program XReitan. The atomic coordinates position from which it was obtained in the case of Example 1-1 as an example is shown in Table 1.

[0028]

[Table 1]

原子	サイト	席占有率	X	Y	Z
Li	3a	0.99071	0	0	0
Ni	3a	0.00929	0	0	0
Li	3b	0.01182	0	0	0.5
Ni	3b	0.82019	0	0	0.5
Co	3b	0.16799	0	0	0.5
O	6c	1.0	0	0	0.24207

[0029]Distortion ODP of octahedron was calculated based on the following expression.

[Equation 1]

$$ODP = d_{0-0, intra} / d_{0-0, inter}$$

ただし、 $d_{0-0, intra} = a$

$$d_{0-0, inter} =$$

$$\sqrt{(a^2/3) + [(c/6) - 2c(0.25 - Z)]^2}$$

Z shows here the X coordinate position of the oxygen atom for which it asked in the Rietveld analysis, and the value is shown in the Z column of Table 1. Similarly the X column and the Y column show the position of an X coordinate and a Y coordinate among Table 1, a and c are the grating constants of an a-axis and c axis, respectively.

[0030]A 3a site non-Li-ion mixing rate, a grating constant, and ODP are collectively shown in Table 2. Example 1-2, 3, and the comparative examples 1-3 asked for the oxygen coordinates atom position similarly, and calculated a 3a site non-Li-ion mixing rate, a grating constant, and ODP. A result is collectively shown in Table 2.

[0031][Cell examination] The cell was produced as follows using the obtained active material, and charge-and-discharge capacity was measured. Acetylene black 6wt% and PVDF(poly **-ized vinylidene)9wt% was mixed to active-material-powder 85wt%, and NMP (n-methyl pyrrolidone) was added and pasted. It applies so that the active material weight after drying this in the expanded metal mesh made from aluminum may become $0.07\text{g}/\text{cm}^2$, and it dries. Vacuum drying was performed at 120 more **, and it was considered as the anode. The equivalent mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) which makes LiPF_6 of 1M an electrolysis solution for Li metal with a supporting electrolyte was used as a negative electrode. It assembles in the glove box of Ar atmosphere on the beaker cell shown in drawing 2. The produced cell was neglected for about 10 hours, after open circuit voltage (OCV) was stabilized, made current density to an anode $1.0\text{ mA}/\text{cm}^2$, and did the charge and discharge test by cutoff 4.3-3.0V. A result is shown in Table 2. However, a capacity maintenance rate (%) is $100 \times (100\text{th service capacity}) / (1\text{st service capacity})$.

It comes out.

[0032]

[Table 2]

試料	3aサイト混入率 (%)	a軸格子定数 (Å)	c軸格子定数 (Å)	ODP	1 回目放電容量 (mAh/g)	容量維持率 (%)
実施例 1-1	0.83	2.8696	14.1673	1.060	188.2	97.5
1-2	0.93	2.8638	14.1531	1.055	191.4	97.9
1-3	0.79	2.8649	14.1592	1.058	189.0	98.9
1-4	0.99	2.8645	14.1581	1.060	192.3	98.3
比較例 1-1	1.70	2.8676	14.1631	1.071	185.5	99.7
1-2	0.82	2.8666	14.1603	1.070	189.4	99.8
1-8	1.88	2.8626	14.1519	1.068	187.3	94.5

As shown in Table 2, the non-Li-ion mixing rate of 3a site of an active material is 2% or less, and when the value of ODP is 1.065 or less range, it turns out that the cell by which service capacity has the high performance of a capacity maintenance rate highly is obtained.

[0033] Although the cell in this example was a cell which uses Li metal as a negative electrode, use of the active material of this invention is not limited to this, and Li can also use for a negative electrode reversibly the carbon which can be intercalated, such as a carbon fiber and graphite, by a cell reaction.

[0034]— It replaces with the nickel cobalt coprecipitation hydroxide used in Example 1 as the end of example 2—[composition of active material sample] precursor powder, Formula: (nickel_{1-x-y}Co_xMn_y) (OH)_n. It compounded like Example 1 except having used the nickel cobalt manganese coprecipitation hydroxide prepared so that x and y might become a value shown in ** thru/or ** of the following, respectively in

[0035]** Example 2-1 x=0.16, y= 0.04, Li/(nickel+Co+Mn) =1.0, synthesizing temperature =700 **** example 2-2 x=0.10, y= 0.10, Li/(nickel+Co+Mn) =1.0, and the synthesizing temperature =700 **** example 2-3. x= 0.15, y= 0.10, Li/(nickel+Co+Mn) =1.0, synthesizing temperature =700 **** example 2-4 x=0.20, y= 0.05, Li/(nickel+Co+Mn) =1.0, and synthesizing temperature =700 **** comparative example 2-1 x=0, y= 0.20, Li/(nickel+Co+Mn) =1.0, synthesizing temperature =700 **** comparative example 2-2 x=0.16, y= 0.04, Li/(nickel+Co+Mn) =1.0, synthesizing temperature =780 **** comparative example 2-3 x=0.10, y= 0.10, Li/(nickel+Co+Mn) =1.0, synthesizing temperature = 650 ** [0036][X diffraction] It analyzed by measuring the X-ray diffraction pattern of an active material sample like Example 1. The atomic coordinates position in Example 2-1 is shown in Table 3. In this analysis, although the mixing metal ion of 3a site was used only as nickel ion, even when cobalt, manganese, and three ion of nickel mix, in order to be able to obtain the same analysis result and to investigate distortion of a crystal, an error is not produced.

[0037]

[Table 3]

原子	サイト	占有率	X	Y	Z
Li	3a	0.98952	0	0	0
Ni	3a	0.01048	0	0	0
Li	9b	0.00551	0	0	0.5
Ni	9b	0.78559	0	0	0.5
Co	3b	0.14971	0	0	0.5
Mn	9b	0.05978	0	0	0.5
O	6c	1.0	0	0	0.24267

[0038] Distortion ODP of octahedron was calculated like Example 1. A 3a site non-Li-ion mixing rate, a grating constant, and ODP are collectively shown in Table 4. Although the grating constant used the result depended on the Rietveld analysis, evaluation is possible even if it uses the value by the usual grating constant measurement, in order to calculate c/a.

[0039][Cell examination] Using the obtained active material, the cell was produced like Example 1 and charge-and-discharge capacity was measured. A result is shown in Table 4.

[0040]

[Table 4]

試料	3aサイト混入率 (%)	a軸格子定数 (Å)	c軸格子定数 (Å)	c/a	ODP	1 回目放電量 (mAh/g)	容量維持率 (%)
実施例2-1	1.05	2.8652	14.1614	4.949	1.055	192.5	97.3
2-2	1.27	2.8696	14.1796	4.941	1.058	193.3	97.5
2-3	1.52	2.8671	14.1749	4.944	1.052	191.6	98.1
2-4	0.89	2.8653	14.1622	4.949	1.055	189.6	98.4
比較例2-1	1.75	2.8806	14.1966	4.928	1.065	179.1	93.3
2-2	1.26	2.8657	14.1693	4.944	1.072	188.4	91.6
2-3	1.01	2.8695	14.1839	4.949	1.068	192.7	91.3

[0041]Some nickel is replaced from Co and Mn as mentioned above, and when this invention lithium nickel multiple oxide which controlled ODP or less to 1.060 is used as an active material of a lithium secondary battery, it turns out that the cell by which service capacity has the high performance of a capacity maintenance rate highly is obtained. On the other hand, only by adding Co and Mn, as a comparative example shows, since crystallinity falls, the improvement in a cycle characteristic cannot be obtained.

[0042]- It replaces with the nickel cobalt coprecipitation hydroxide used in Example 1 as the end of example 3-[composition of active material sample] precursor powder, Formula: (nickel_{1-x-y}Co_xAl_y) It compounded like Example 1 except having used the nickel cobalt aluminum coprecipitation hydroxide prepared so that x and y might become a value shown in ** thru/or ** of the following, respectively in (OH)_n. Each synthesizing temperature was 700 **.

[0043]** Example 3-1. x= 0.16, y= 0.03, Li/(nickel+Co+aluminum) =1.0** example 3-2 x=0.11, y= 0.03, Li/(nickel+Co+aluminum) =1.0** example 3-3 x=0.15, y= 0.10, and the Li/(nickel+Co+aluminum) =1.0** example 3-4. x= 0.10, y= 0.10, Li/(nickel+Co+aluminum) =1.0** comparative example 3-1 x=0.10, y= 0.16, Li/(nickel+Co+aluminum) =1.0** comparative example 3-2 x=0.04, y= 0.28, and the Li/(nickel+Co+aluminum) =1.0** comparative example 3-3. x= 0, y= 0.16, Li/(nickel+Co+aluminum) =1.0 [0044] [X diffraction] It analyzed by measuring the X-ray diffraction pattern of an active material sample like Example 1. It is shown in Table 5 by making the atomic coordinates position in Example 3-1 into an example. In this analysis, although the mixing metal ion of 3a site was used only as nickel ion, even when aluminum, cobalt, and three ion of nickel mix, in order to be able to obtain the same analysis result and to investigate distortion of a crystal, an error is not produced.

[0045]

[Table 5]

原子	サイト	占有率	X	Y	Z
Li	3a	0.99274	0	0	0
Ni	3a	0.00726	0	0	0
Li	3b	0.01342	0	0	0.5
Ni	3b	0.77913	0	0	0.5
Co	3b	0.15785	0	0	0.5
Al	3b	0.04960	0	0	0.5
O	6c	1.0	0	0	0.24288

[0046]Distortion ODP of octahedron was calculated like Example 1. A 3a site non-Li-ion mixing rate, a grating constant, and ODP are collectively shown in Table 6. Although the grating constant used the result depended on the Rietveld analysis, evaluation is possible even if it uses the value by the usual grating constant measurement, in order to calculate c/a.

[0047][Cell examination] Charge-and-discharge capacity was measured like Example 1 using the obtained active material. A result is shown in Table 6.

[0048]

[Table 6]

試料	3a/4b 混入率(%)	a 軸格子定数(Å)	c 軸格子定数(Å)	c/a	ODP	1 回目放電容量mAh/g	容量維持率(%)
実施例3-1	0.73	2.8627	14.1700	4.950	1.054	189.8	98.4
3-2	1.81	2.8630	14.1764	4.952	1.056	194.1	97.5
3-3	1.56	2.8614	14.1878	4.951	1.053	191.8	97.7
3-4	1.61	2.8673	14.1720	4.942	1.053	188.9	98.3
比較例3-1	2.91	2.8580	14.2851	4.963	1.060	175.2	96.5
3-2	1.82	2.8501	14.1927	4.980	1.060	171.8	97.2
3-3	1.97	2.8634	14.2027	4.960	1.063	159.7	98.1

[0049]Some nickel is replaced with Co and aluminum as mentioned above, and when this invention lithium nickel multiple oxide which controlled ODP or less to 1.058 is used as an active material of a lithium secondary battery, it turns out that the cell by which service capacity has the high performance of a capacity maintenance rate highly is obtained. On the other hand, the capacity of that whose cycle characteristic of a cell improves will fall only by adding Co and aluminum, as a comparative example shows.

[0050]

[Effect of the Invention]It is effective in the rechargeable battery which excelled [use / the lithium cobalt double oxide by this invention / as positive active material of a nonaqueous secondary battery] in the capacity maintenance rate being producible, and according to the method of evaluation of this invention, it is possible to measure the characteristic of the positive active material for nonaqueous secondary batteries simple and certainly. Therefore, if an active material is evaluated using an active material of this invention, and a valuation method for the same and a cell is assembled based on it, it is possible to obtain a highly efficient lithium secondary battery easily.

[Translation done.]